

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Improvements in or relating to the Manufacture of Organic Colouring Materials

We, E. I. DU PONT DE NEMOURS AND Co., of Wilmington, Delaware, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of water-insoluble organic colouring matters. The invention relates more particularly to the manufacture of water-insoluble organic colouring matters such as those of the phthalocyanine and vat classes.

It is well known that water-insoluble organic colouring matters when dissolved in the acids usually employed for the acid pasting can be precipitated in crystalline form by diluting the acid solution with water. Where the dilution is carried out slowly the colouring matter is obtained in the form of large crystals which are of little or no value as pigments. Water-insoluble organic colouring matters or organic pigments are therefore generally precipitated from the acid solution by the process known as "drowning", that is, by running the acid solution of the colouring matter into a relatively large volume of water while the water is being agitated.

According to the present invention water-insoluble organic colouring matters, such as phthalocyanines and vat colouring matters, are manufactured by a process comprising precipitating the colouring matter from an acid solution by introducing the latter into an aqueous fluid which is in a state of turbulent flow.

By turbulent flow or turbulence we refer to the motion of a liquid flowing through a pipe at a velocity greater than its critical velocity, which is distinguished from the straight line or laminar flow by the presence of innumerable eddy currents (see "Principles of Chemical Engineering" by Walker, Lewis and McAdams, Second Ed. (1927), pages 73—77). The said turbulence is also to be distinguished from agitation in which air is incor-

porated with the liquid to cause a foam or froth.

Because of the innumerable eddy currents which characterise turbulence, the acid solution flowing into the water in turbulent flow is instantaneously diluted to a point where crystal growth is retarded or prevented, while in the usual drowning with ordinary types of agitation the mass of the liquid is merely rotated with practically no eddy current. Thus by working according to the invention water-insoluble organic colouring matters such as phthalocyanines and vat colouring matters, are obtained, which are in an extremely fine state of subdivision and exhibit improved brilliance and tinctorial strength.

The drowning medium may be water, dilute acids, aqueous solutions of inorganic salts or of organic compounds in which the acids used for dissolving the pigments are soluble and in which the pigments are insoluble.

Any water-insoluble organic colouring matter that is soluble in the usual acid-pasting acids, such as oleum, sulphuric acid, chlorosulphonic acid, ethylsulphuric acid, phosphoric acids, para-toluenesulphonic acid, etc., may be crystallised out in fine form by drowning according to this process.

The acid solution of the colouring matter may be introduced into any tube in which turbulence exists either counter-current, co-current or at any other angle with the flow of the diluting liquid. Or turbulence may be created in other ways. For example, the acid solution of the organic pigment may be introduced into a centrifugal or impeller pump, which becomes merely a modified turbulence tube due to the flow of the liquid through or by the impeller tubes or vanes, or passed to a high speed propeller operating in a confined space.

The following examples are given to illustrate the invention. The parts used are by weight unless otherwise designated.

## EXAMPLE 1.

60 Parts of N:N'-diethyl-2:2'-di-

pyrazolanthranyl, are dissolved in 600 parts of 98% sulphuric acid. One half (A) of the acid solution is drowned in 3000 parts of water at 90°—95° C. by adding the acid solution of the water in several small streams with good agitation. The other half (B) is introduced according to the invention into a stream of water flowing through a constricted tube at above the critical velocity, by a small pipe centrally placed in the larger constricted tube and parallel to it, extending through the constriction and ending where the larger tube resumes its original size. The acid solution is run into the water in the direction of flow. The acid solution is thus drowned at 25°—30° C., at a water-acid ratio of 30 to 1.

Both precipitates (A and B) are filtered off, washed acid-free and dried. The (B) product is much darker in mass tone, much yellower and much brighter and stronger than the (A) product.

#### EXAMPLE 2.

50 Parts of mono-chlorinated indanthrone are dissolved in 500 parts of 98% sulphuric acid. One half (A) of the acid solution is added slowly to 2500 parts of water at 85°—95° C. under agitation. The other half (B) is drowned according to the invention by passing into water in turbulent flow downward through a tube ten inches long and  $\frac{1}{4}$  inch in diameter having a constriction to  $\frac{1}{8}$  inch about two inches from the outlet, the acid inlet being  $\frac{1}{8}$  inch pipe centrally arranged in the turbulence tube and discharging at the outlet side of the constriction. The flow of water through the constriction is 12 to 15 feet per second. The temperature is 77°—82° C. and the water-acid ratio is 30 to 1. The two suspensions are treated as in Example 1. The (B) product is found to be lighter in mass tone, redder and much stronger than the (A) product.

#### EXAMPLE 3.

50 Parts of flavanthrone are dissolved in 500 parts of 98% sulphuric acid. One half (A) of the acid solution is drowned slowly in 2500 parts of water under agitation at 30°—40° C. The other half (B) is drowned as described for (B) in Example 1. Both suspensions are filtered and washed acid-free. The nutsch cakes are treated with 3% aqueous sodium hypochlorite solution to "bleach", i.e. purify the product, filtered, washed free from hypochlorite and dried. The (B) product is very brown in mass tone, very red and bright and much stronger than the (A) product.

#### EXAMPLE 4.

50 Parts of indanthrone are dissolved in 500 parts of 98% sulphuric acid. This solution is divided into two equal parts

which are treated as described in Example 3, except that in both cases the drownings are carried out at 80°—90° C. In this case the (B) product is very light in mass tone, redder, brighter and much stronger than the (A) product.

#### EXAMPLE 5.

60 Parts of copper phthalocyanine (see B.P. 410,814, Example 3) are dissolved in 600 parts of 98% sulphuric acid. One half of the solution (A) is added to 3000 parts of water under good agitation at 25°—30° C. The other half (B) is drowned as described under (B) in Example 1. Both parts are filtered, washed acid-free and the nutsch cakes reslurried with dilute ammonia. The charges again are filtered, washed alkali-free and dried. The (B) product is very dark in mass tone, redder, brighter and stronger than the (A) product. The acid-water ratio can be varied from 1:10 to 1:100, with similar results.

#### EXAMPLE 6.

Where the above example is repeated, except that the drowning of both parts is carried out at 95°—100° C., the (B) product is darker in mass tone, redder, brighter and stronger than the (A) product.

#### EXAMPLE 7.

60 Parts of "Sulphanthrene" Orange R, Colour Index No. 1217, are added to 600 parts of sulphuric acid monohydrate. The solution is drowned in two parts and worked up as described in Example 1, at 90°—95° C. for both parts. The (B) product is darker in mass tone, very red, very bright and much stronger than the (A) product.

#### EXAMPLE 8.

Example 7 is repeated using "Sulphanthrene" Red 3B, Colour Index No. 1212. The (B) product is redder in mass tone, very yellow in shade and much stronger than the (A) product.

#### EXAMPLE 9.

150 Parts of copper phthalocyanine are dissolved in 1500 parts of 98% sulphuric acid. One-half of the acid solution is added to 7500 parts of water under good agitation at 25°—30° C. The other half is introduced into an impeller pump at 25°—30° C. instead of a tube as described in Example 1. Both suspensions are treated as in Example 1. The product from the pump is much darker in mass tone, brighter and much stronger than the other.

#### EXAMPLE 10.

50 Parts of 2:1-naphth-thioindigo are dissolved in 1250 parts of 98% sulphuric acid at 5° C. When drowned in the tube described in Example 1 (B) with the water at 3° C., there is a temperature rise of 5° C. and the liquor contains 3.1% sul- 130

phuric acid. The resulting suspension is filtered and washed, and compared with a control prepared by drowning by slow addition to well agitated water.

- 5 The product prepared by the method of this invention is much stronger and brighter in shade than the control product.

#### EXAMPLE 11.

- 10 50 Parts of Bz-3:Bz-4-dichloroanthraquinone-2:1(N)-benzacidone are dissolved in 500 parts of 98% sulphuric acid below 50° C. and drowned at a uniform rate in water at 90° C. in the apparatus described  
15 in Example 1 (B). The temperature after leaving the tube is 92° C. and the liquor contains 3.8% sulphuric acid. After filtering and washing acid-free the resulting stiff paste is thinned by the addition  
20 of a small amount of the formaldehyde condensation product of naphthalene sulphonic acid and incorporated in emulsion printing inks. The prints are much stronger and brighter than those from a  
25 control preparation obtained by drowning by slow addition to well agitated water.

#### EXAMPLE 12.

- 60 Parts of disodium phthalocyanine (described in B.P. 410,814) are dissolved  
30 in 600 parts of 98% sulphuric acid at 0° C. One-half of the solution (A) is drowned by adding to 3000 parts of water at 25—30° C. under agitation. The other  
35 half (B) is drowned through the tube as described in Example 1. Both parts are filtered, washed acid-free and dried. Thus metal-free phthalocyanine is obtained. The (B) product is darker in mass tone,  
40 very bright and very strong compared with the (A) product.

#### EXAMPLE 13.

- 60 Parts of aluminium phthalocyanine are acid-pasted and drowned in a turbulence tube in the same manner as described  
45 in Example 1. The product exhibits great brightness and strength.

#### EXAMPLE 14.

- 60 Parts of copper phthalocyanine are dissolved in 600 parts of anhydrous phosphoric acid at 90°—100° C. The charge  
50 is divided into two parts which are drowned as described in Example 1, but at 95°—100° C. for both parts. The tube

drowned product is superior to the other product in both brilliancy and strength. 55

#### EXAMPLE 15.

60 Parts of hexa-decachloro-copper phthalocyanine (as described in B.P. 478,256) are dissolved in 600 parts of a 3 to 1 mixture of sulphuric acid mono-  
60 hydrate and chlorosulphonic acid. The charge is divided into two parts and drowned as in Example 1, except that both parts are drowned at 25—30° C. The  
65 tube drowned product is darker in mass tone, bluer, brighter and stronger than the other.

#### EXAMPLE 16.

404 Parts of crude copper phthalocyanine containing anhydrous sodium sulphate 70 (120 parts of copper phthalocyanine) are dissolved in 2100 parts of 98% sulphuric acid. The acid solution is drowned into water at 95—98° C. in a state of turbulent flow through a one inch pipe 19  
75 inches long, the acid inlet pipe (1/4") being arranged coaxially therewith and extending into the one inch pipe in the direction of flow of the diluting water five inches. The ratio of volumes of flow of diluting  
80 liquid:acid is 30:1. The resulting pigment is very bright and strong.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to  
85 be performed, we declare that what we claim is:—

1. Process for the manufacture of water-insoluble organic colouring matters such as phthalocyanines and vat colouring  
90 matters, comprising precipitating the colouring matter from an acid solution by introducing the latter into an aqueous fluid which is in a state of turbulent flow.

2. Process for the manufacture of 95 water-insoluble organic colouring matters substantially as described in the foregoing Examples.

3. Water-insoluble organic colouring matters whenever manufactured by the 100 process claimed in Claim 1 or 2 or by an obvious chemical equivalent thereof.

Dated the 21st day of February, 1941.

J. W. RIDSDALE,  
Solicitor for the Applicants.

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